Wetting Transitions of Binary Liquid Mixtures at a Weakly Attractive Substrate

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Abstract

The adsorption of a binary liquid mixtures onto a weakly attractive substrate has been studied in the vicinity of bulk liquid phase separation. A wetting transition between two different kinds of wetting films has been found. Below the wetting transition temperature, homogeneous films of one liquid phase wet the substrate. Above the wetting temperature, the wetting films contain both liquid phases. The surface phase transition line associated with this wetting transition is found to extend to both sides of the bulk phase separation line. On one side it is a prewetting line, and on the other side it becomes a line of triple point induced dewetting transitions. The experimental system used to study this behavior was liquid helium mixtures on a cesium substrate.

Keywords

Interfacial tension, liquid-liquid equilibria, mixture, triple point, wetting.

1.0 Introduction

Liquid helium has an extensive history in the study of wetting, particularly since 1991 when Cheng, Cole, Saam and Treiner [1] predicted that ⁴He would not wet cesium at zero temperature and should therefore undergo a wetting transition at some higher temperature. These predictions were quickly verified and led to the first measurements of the complete phase diagram associated with a first order wetting transition [2]. The experiment reported here examines the wetting behavior of ³He-⁴He mixtures on cesium near bulk phase separation. It provides the first observations of triple point induced dewetting transitions and reveals a connection between wetting, prewetting, and triple point dewetting transitions that should be a general feature of binary liquid wetting.

The question central to the study of wetting is what will happen on a surface when there is a phase transition in the bulk. We will address this question by considering the situation of an inert solid substrate suspended in the saturated vapor above a bulk liquid, and by examining the nature of the adsorbed liquid film that forms on the substrate at equilibrium. For a simple liquid there are two possibilities. Either very little or no adsorbtion will take place in which case the substrate is said to be non-wet, or a macroscopically thick film of liquid will form on the substrate in which case it is said to be wet. For the wetting case the thickness of the adsorbed film is limited only by gravity and the height of the substrate above the liquid. A wetting transition is typically a first order transition that occurs on the surface between the non-wet state and the wet state.

In binary liquid mixtures, two distinct liquid phases (like oil and water) can coexist with each other and with the vapor. Consequently, the wetting behavior is somewhat richer. In this case there are five possibilities for the adsorbed film: The substrate can be non-wet, or it can be wet by one liquid or by the other liquid. In addition, there are two possible adsorbtion states in which thick

wetting layers of both liquid phases are found on the substrate. For phase separated binary liquid mixtures, there are two different kinds of wetting transitions that can occur on the substrate: a wetting transition from a non-wet state to a wet state, or a wetting transition from a wetting film state containing only one liquid phase to a state in which the wetting film contains layers of both liquid phases. This second kind of wetting transition occurs between two different kinds of wetting films. The helium/cesium system contains examples of both kinds of wetting transitions. This paper will focus on the wetting behavior of helium mixtures near bulk liquid phase separation and will explore the consequences of a wetting transition of the second type, between two different kinds of wetting films.

The bulk helium mixture phase diagram is shown schematically in the T vs. X_3 phase diagram of figure 1, where T is the temperature and X_3 is the concentration of 3 He in the bulk liquid. The bold solid curve is the bulk liquid phase separation curve. To the left of this curve, the 4 He rich liquid phase coexists with the vapor, and to the right of this curve, the 3 He rich liquid coexists with the vapor. In the region beneath the phase separation curve, both liquids coexist with each other and with the vapor. For phase separated helium mixtures, it is well established that there is always a thick wetting layer of the 3 He rich liquid between the 4 He rich liquid and the vapor [3]. Therefore, of the five possible adsorption states described in the previous paragraph, only three are possible for phase separated helium mixtures: non-wetting films; wetting films of the 3 He rich liquid; and films which contain a wetting layers of both liquids, with the 4 He rich liquid near the substrate and the 3 He rich liquid near the vapor.

Our results are summarized by the dashed lines of Fig. 1. We have found a wetting transition in the phase separation region between two different kinds of adsorbed films with T_w =0.54 K. This wetting transition is first order and has the usual associated prewetting line

extending to higher temperatures in the ³He rich region of the phase diagram. In addition, there is a dewetting line associated with the wetting transition which extends from the wetting transition downward in temperature on the ⁴He rich side of the phase diagram. In the region of the phase diagram between the dewetting line and the bulk phase separation line, the substrate is non-wet.

2.0 Experimental Results

Our experimental techniques are similar to those we used to study adsorption in other systems and have been described previously [2]. The experimental apparatus consists of an OFHC vacuum can which is suspended from the bottom of a dilution refrigerator. Two quartz crystal microbalances [4] are contained within the can. Cesium is evaporated from a pure metallic source

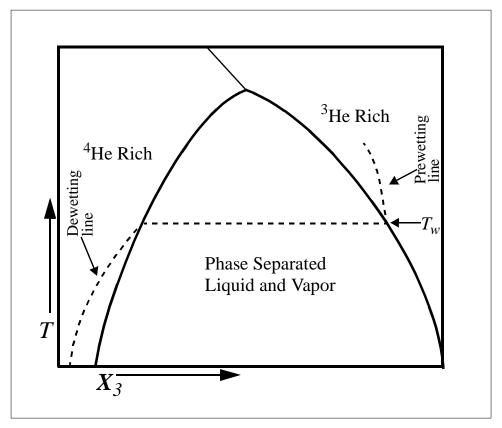


Fig. 1 The T vs. X_3 phase diagram for helium mixtures on cesium. For clarity, the phase diagram is not drawn to scale. The bulk three phase region is the region beneath the bold solid line. The dashed lines indicate phase transitions in the adsorbed film.

onto the mass sensitive regions of one of the microbalances. Bulk 3 He- 4 He liquid mixture fills the bottom of the can so that the microbalances are suspended in the saturated vapor above the liquid. Under these conditions a film of liquid is adsorbed on the microbalance causing a shift, $-\Delta f$, of the resonant frequency relative to its value in vacuum. The sensitivity of the microbalance is approximately 0.133 Hz/monolayer of liquid 3 He. The microbalance oscillates in a shear mode, so it is insensitive to the superfluid component of the films. In the temperature range of this experiment, virtually all of the 4 He in the 4 He rich liquid phase is superfluid, so $-\Delta f$ is essentially a measure of the 3 He content of the films.

Our results consist of measurements of $-\Delta f$ as a function of the temperature of the experiment cell, T, and the concentration of 3 He in the bulk liquid, X_3 [5]. Care was taken to insure that the liquid was well mixed and equilibrated before each run was started, and that a sufficient quantity of liquid was present so that the fraction of helium atoms in the vapor was always less than 5×10^{-3} of the total, so that X_3 is constant along the experimental trajectories to within 0.003. Because of limitations on the length of this paper, it is not possible to include the complete set of arguments leading to the conclusions presented here. A more detailed description of these results is published elsewhere [6,7].

Figure 2 shows the results of a measurement made with a mixture composed of approximately equal parts 3 He and 4 He, so that both liquid phases were present in the bulk for the temperature range of the measurement. At high temperatures the substrate was wet by a thick 4 He rich superfluid film [8] which, as always, was wet by a layer of the 3 He rich liquid between the superfluid and the vapor [3] so that the wetting film contains both liquid phases. As the temperature was decreased, there was a sharp, hysteretic transition at T \sim 0.5 K to a state with a greater frequency shift, indicating an increase of the 3 He content of the film. Through consideration of the data shown

in Figs. 2-4 and from the behavior of the frequency shift as the experiment was cooled from \sim 4 K, this low temperature state can be identified as a wetting film composed of only the 3 He rich liquid. The transition is a first order wetting transition between two different kinds of wetting films: homogeneous 3 He rich films at low temperature, and films containing a thick layer of each of the liquid phases at high temperatures. A simple argument identifies the top branch (triangles in Fig. 2) of the hysteresis loop as the stable one and the wetting temperature as the upper closing point of the loop, $T_w = 0.54$ K. The cesium is deposited only on a circular patch in the middle of each face of the microbalance. The surfaces of the quartz microbalance which are not coated with cesium are strongly binding surfaces and are therefore always wet by films which contain both liquid phases

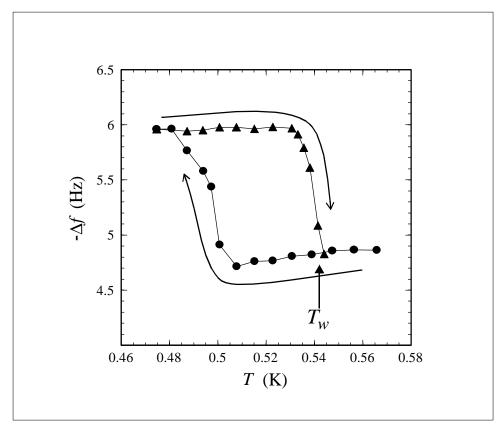


Fig. 2 Wetting transition measurement. This wetting transition is a first order transition between two different kinds of wetting films: ³He rich liquid films at low temperature, and films which contain layers of both liquid phases at high temperature. Data taken while warming is plotted as triangles and data taken while cooling is plotted as circles.

[9]. These films at the boundaries of the cesium serve to nucleate transitions to similar films on the cesium.

First order wetting transitions are accompanied by lines of prewetting transitions [10,11]. In this case, the prewetting line should extend upward in temperature from T_w , on the ³He rich side of the bulk phase separation line. Figure 3 shows the data for the measurements of this prewetting line. For clarity, the data sets for each concentration are shifted vertically with respect to each other, and plotted as a function of T- T_s , where T_s is the bulk liquid phase separation temperature for that

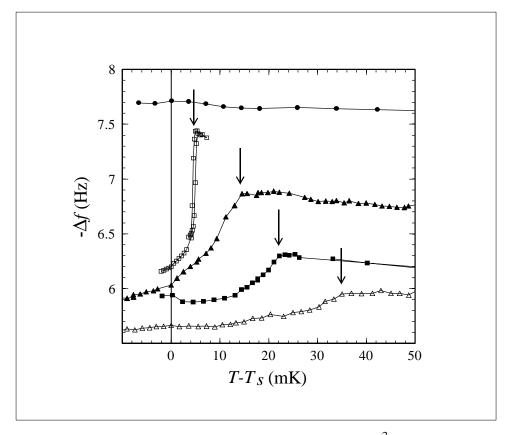


Fig. 3 Prewetting line measurements. At high temperatures, a thick 3 He rich liquid film wets the substrate. Closer to T_{s} , a layer of 4 He rich liquid forms near the substrate so that the wetting film contains both liquid phases. The growth of this 4 He rich layer occurs in a steep jump (marked with arrows) at the prewetting transition. Data was taken with mixtures of $X_{3} = 0.905$ (filled circles), 0.873 (open squares), 0.775 (filled triangles), 0.747 (filled squares), and 0.726 (open triangles).

concentration. For temperatures far above T_s , the substrate was wet by a thick film of ${}^3\mathrm{He}$ rich liquid. As the experiment was cooled toward T_s , a sharp break in the slope of the curves was found. These abrupt changes in slope of the data of Fig. 3 locate the prewetting transitions between homogeneous, ${}^3\mathrm{He}$ rich wetting films at high temperatures, and ${}^3\mathrm{He}$ rich films with a layer of ${}^4\mathrm{He}$ rich liquid at the substrate at low temperatures. The X_3 =0.873 (open squares) prewetting transition was hysteretic, though its width, 0.6 mK, was much smaller than that of the wetting transition. The prewetting transitions were found to move monotonically closer to T_s as the ${}^3\mathrm{He}$ concentration was increased until the prewetting line intersects with the bulk phase separation line at T= T_w . For the X_3 =0.905 (solid circles) mixture, T_s < T_w , so no transition occurred.

We also measured the temperature dependence of $-\Delta f$ in the ⁴He rich liquid region of the bulk phase diagram for a range of ³He concentrations between 0.09 and 0.4. The results are shown in Fig. 4. Again, the data sets for each concentration are shifted vertically with respect to each other, and plotted as a function of T- T_s . At the highest temperatures for each mixture, far from the bulk triple line, previous experiments [8,12,13], and the behavior of the films as they were cooled from ~4 K indicate that the substrate was wet by a thick superfluid ⁴He rich film covered by a layer of ³He [3]. As the temperature was lowered toward T_s the frequency shift increased slightly as the ³He rich layer on top became thicker. This trend continued until a point, near but still above T_s , where there was a sharp drop in $-\Delta f$, which was followed by a rapid but continuous increase of $-\Delta f$ as the temperature was further cooled toward T_s . For $T < T_s$, $-\Delta f$ became nearly constant. When the direction of the temperature sweeps was reversed, the behavior of the adsorbed films was found to be hysteretic. The observed hysteresis loops are clear signatures of a first order phase transition in the adsorbed films. They are triple point induced dewetting transitions [14,15]. These results are the first experimental observations of triple point induced dewetting, and confirm the prediction of

Petersen and Saam that triple point dewetting should occur in this system [16].

Triple point induced dewetting occurs as a result of the competition between the two different kinds of films to wet the substrate. For $T < T_w$, homogeneous, 3 He rich films wet more strongly than films composed of both liquids. Just slightly to the 4 He rich side of the phase separation curve of Fig. 1, the 3 He rich films remain on the substrate. However, in this region of the phase diagram, the 3 He rich liquid is not stable as a bulk phase. Consequently, the films cannot

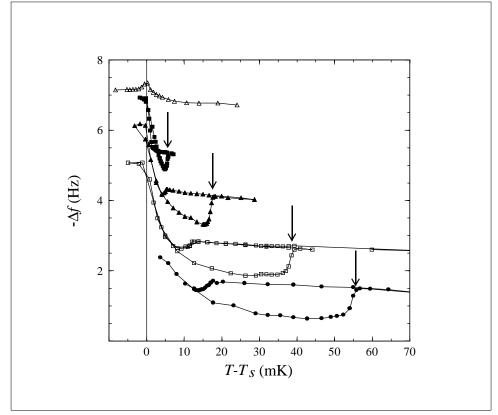


Fig. 4 Dewetting line measurements. At high temperatures, the substrate is wet by films of 4 He rich liquid with a thin layer of 3 He rich liquid on top. For $T < T_s$, the substrate is wet by films of 3 He rich liquid. At intermediate temperatures, 3 He rich films remain on the substrate, but the 3 He rich liquid is not stable as a bulk phase, so the substrate is non-wet. The triple point induced dewetting transitions (marked with arrows) are first order transitions between the high temperature wetting state and the intermediate temperature non-wetting state. Data was taken with mixtures of $X_3 = 0.091$ (filled circles), 0.110 (open squares), 0.152 (filled triangles), 0.197 (filled squares), and 0.395 (open triangles).

be macroscopically thick, and so the substrate is non-wet. Far from the phase separation curve, the energetic cost of stabilizing a layer of the ³He rich phase is too great, and the ⁴He rich liquid wets the substrate. The triple point dewetting transition marks a point of coexistence of the ⁴He rich wetting films and the ³He rich non-wetting films. The interplay between the weakly attractive substrate potential, the surface tensions, and the costs of stabilizing liquids that are unstable in bulk determines the position of the dewetting transition as is described in Refs.[15,16].

The two liquids and the vapor of a binary liquid system do not coexist at a single triple point, but along a line of triple points. Consequently, there can be a line of triple point induced dewetting transitions, or a dewetting line. As can be seen in Fig. 4, for successively richer 3 He mixtures the dewetting transitions move monotonically closer to T_s , until the dewetting line intersects with the bulk phase separation line at the wetting transition. For the X_3 =0.395 mixture, $T_s > T_w$, so no transition was observed.

3.0 Conclusions

The wetting transition and its associated prewetting line on the right side of Fig. 1 form the usual phase diagram of a first order wetting transition, examples of which have been found recently in several experiments [2,17,18,19]. The extension of the surface phase transition as a dewetting line on the other side of the bulk triple line, however, has not been previously observed. Previous experiments have studied either systems of only two coexisting bulk phases [2,18,19], or the wetting of one bulk phase at the interface between two others [17]. The experiment reported here differs from previous work in that it examines a wetting transition at a substrate near a region of three coexisting bulk phases. As a result, there are two different bulk phases which can wet the substrate. This experiment has demonstrated that a wetting transition between two different kinds of wetting films will not only have a prewetting line associated with it, but will also have a line of

triple point induced dewetting transitions, or a dewetting line, associated with it.

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